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Declaration under Rule 4.17:

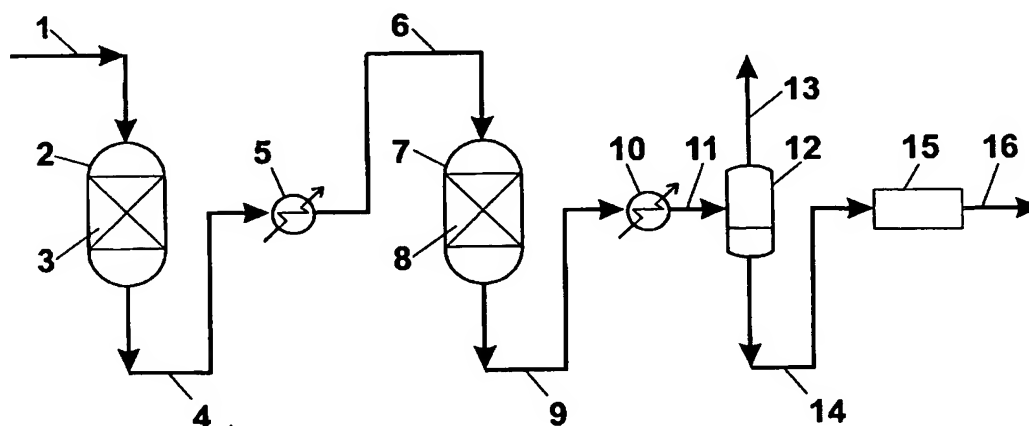
— of inventorship (Rule 4.17(iv)) for US only

Published:

— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

[Continued on next page]

(54) Title: PROCESS FOR SYNTHESIS OF METHANOL



(57) Abstract: The invention provides a process for production of methanol from a feed stream rich in hydrogen carbon monoxide and carbon dioxide. The feed stream is converted to a converted process stream comprising methanol and small amounts of higher alcohols, aldehydes and ketones in the presence of a catalyst active in conversion of hydrogen and carbon monoxide into methanol. The converted process stream is cooled to a cooled process stream to 20-200°C. The cooled process stream is hydrogenated into a hydrogenated process stream rich in methanol and depleted in aldehydes and ketones in presence of a hydrogenation catalyst. The catalyst is active in conversion of aldehydes and ketones into alcohols in a process stream rich in methanol and further comprising hydrogen, carbon monoxide and carbon dioxide. The hydrogenated process stream is cooled to a cooled, condensed process stream, and subsequently the cooled, condensed process stream is separated into a gas phase and a liquid crude methanol phase.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 03/13942

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C29/151 C07C31/04 B01J23/72 //F02C3/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C B01J F02C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal, CHEM ABS Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	US 6 723 886 B1 (ALLISON JOE D ET AL) 20 April 2004 (2004-04-20) claims 1-10	1-9
X	EP 0 501 331 A (AIR PROD & CHEM) 2 September 1992 (1992-09-02) claims 1,19,24	1-9
X	WO 95 19844 A (KAO CORP ;TSUKADA KIYOSHI (JP); HATTORI YASUYUKI (JP); MIMURA TAKU) 27 July 1995 (1995-07-27) claims 12,13	1-9
X	EP 0 483 919 A (SHELL INT RESEARCH) 6 May 1992 (1992-05-06) claims 1-11; figures 1,2	1-9
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

4 June 2004

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27. 08. 2004

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 682 002 A (METALLGESELLSCHAFT AG) 15 November 1995 (1995-11-15) claims 1-10; figure 1 ---	1-9
X	EP 0 790 226 A (METALLGESELLSCHAFT AG) 20 August 1997 (1997-08-20) figure 1 claims 1-7 ---	1-9
X	US 4 766 154 A (BONNELL LEO W ET AL) 23 August 1988 (1988-08-23) claims 1-3 ---	1-9
X	US 5 753 194 A (BENZ UWE ET AL) 19 May 1998 (1998-05-19) figure 8 ---	1-9
A	EP 0 970 939 A (MITSUBISHI GAS CHEMICAL CO ;MITSUBISHI HEAVY IND LTD (JP)) 12 January 2000 (2000-01-12) figure 1 ---	1-9
A	WO 01 17936 A (KRUPP UHDE GMBH ;BAEHNISCH HANS JOACHIM (DE)) 15 March 2001 (2001-03-15) figure 1 ---	1-9
A	WO 99 03807 A (ABBOTT PETER EDWARD JAMES ;ICI PLC (GB)) 28 January 1999 (1999-01-28) claims 1-5 ---	1-9
A	EP 0 448 019 A (TOPSOE HALDOR AS) 25 September 1991 (1991-09-25) figure 4 ---	1-9
A	EP 1 010 464 A (AGENCY IND SCIENCE TECHN) 21 June 2000 (2000-06-21) claims 1-13 ---	1,8
A	US 6 303 535 B1 (KAIZIK ALFRED ET AL) 16 October 2001 (2001-10-16) column 5 -----	1-9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 03/13942

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claim : 2 and part of 1

directed to a process for the production of methanol,
wherein the converted process stream is cooled to 80-150C.

2. Claim : 3 and part of 1

directed to a process for the production of methanol,
wherein the hydrogenation (1-c) takes places in a separate
reactor.

3. Claim : 4 and part of 1

directed to a process for the production of methanol,
wherein the hydrogenation (1-c) takes places in a single
reactor.

4. Claim : 5 and part of 1

directed to a process for the production of methanol,
wherein the hydrogenation (1-c) takes places in a tubular
reactor.

5. Claims: 6-7 and part of 1

directed to a process for the production of methanol,
wherein the hydrogenation catalyst is Cu bases catalyst.

6. Claim : 8 and part of 1

directed to a process for the production of methanol,
wherein the hydrogenation catalyst is a noble metal based
catalyst.

7. Claim : 9 and part of 1

and part of 1 directed to a process for the production of
methanol, wherein the hydrogenation catalyst is in the form
of pellets, extrudates, etc

The ISA has carried out a search which relates to inventions
I-VII mentioned above.

The application, hence does not meet the requirements of
unity of invention as defined in Rule 13.1 and 13.2 PCT.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/13942

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6723886	B1	28-11-2002	US 2002177741 A1 WO 02092544 A1 CA 2396581 A1 EP 1231991 A2 WO 0136066 A2 US 2003012711 A1 AU 1769801 A	28-11-2002 21-11-2002 25-05-2001 21-08-2002 25-05-2001 16-01-2003 30-05-2001
EP 0501331	A	02-09-1992	US 5179129 A AU 1131892 A CA 2061710 A1 DE 69202779 D1 DE 69202779 T2 DK 501331 T3 EP 0501331 A2 ES 2075968 T3 JP 5097732 A	12-01-1993 10-09-1992 02-09-1992 13-07-1995 12-10-1995 24-07-1995 02-09-1992 16-10-1995 20-04-1993
WO 9519844	A	27-07-1995	WO 9519844 A1 DE 69414240 D1 DE 69414240 T2 EP 0689477 A1 JP 8507966 T US 5658843 A	27-07-1995 03-12-1998 22-04-1999 03-01-1996 27-08-1996 19-08-1997
EP 0483919	A	06-05-1992	CA 2053578 A1 EP 0483919 A2 JP 4282330 A NO 914220 A ,B, US 5216034 A	30-04-1992 06-05-1992 07-10-1992 30-04-1992 01-06-1993
EP 0682002	A	15-11-1995	DE 4416425 A1 AT 163004 T AU 686754 B2 AU 1792195 A BR 9501949 A CA 2149003 A1 CN 1112912 A ,B DE 59501393 D1 DK 682002 T3 EP 0682002 A1 ES 2113133 T3 GR 3026500 T3 JP 7304698 A NZ 272028 A US 5631302 A ZA 9503783 A	16-11-1995 15-02-1998 12-02-1998 16-11-1995 27-02-1996 11-11-1995 06-12-1995 12-03-1998 30-03-1998 15-11-1995 16-04-1998 31-07-1998 21-11-1995 28-05-1996 20-05-1997 11-11-1996
EP 0790226	A	20-08-1997	DE 19605572 A1 CA 2197574 A1 CN 1163255 A ,B DE 59605046 D1 DK 790226 T3 EP 0790226 A1 IN 186506 A1 US 5827901 A	21-08-1997 16-08-1997 29-10-1997 31-05-2000 07-08-2000 20-08-1997 22-09-2001 27-10-1998
US 4766154	A	23-08-1988	AU 586944 B2	27-07-1989

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/13942

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4766154	A		AU 1113088 A CA 1300175 C JP 63216836 A MX 159833 A	11-08-1988 05-05-1992 09-09-1988 12-09-1989
US 5753194	A	19-05-1998	DE 4420752 A1 DE 4420753 A1 DE 59503581 D1 EP 0687648 A1 US 5672629 A	14-09-1995 21-09-1995 22-10-1998 20-12-1995 30-09-1997
EP 0970939	A	12-01-2000	JP 10204008 A US 5998489 A EP 0970939 A1 DE 69811870 D1 DE 69811870 T2 DK 970939 T3	04-08-1998 07-12-1999 12-01-2000 10-04-2003 16-10-2003 07-04-2003
WO 0117936	A	15-03-2001	DE 19948585 A1 AT 255552 T CN 1372535 T DE 50004668 D1 DK 1210309 T3 WO 0117936 A2 EP 1210309 A2 JP 2003508506 T US 6686398 B1	08-03-2001 15-12-2003 02-10-2002 15-01-2004 15-03-2004 15-03-2001 05-06-2002 04-03-2003 03-02-2004
WO 9903807	A	28-01-1999	AU 8122198 A CA 2293288 A1 EP 0998439 A1 WO 9903807 A1 JP 2001510140 T US 6214314 B1	10-02-1999 28-01-1999 10-05-2000 28-01-1999 31-07-2001 10-04-2001
EP 0448019	A	25-09-1991	DK 71090 A AT 139222 T AU 632406 B2 AU 7351391 A CA 2038530 A1 CN 1055730 A ,B CS 9100722 A2 DE 69120118 D1 DE 69120118 T2 EP 0448019 A2 ES 2090159 T3 JP 2030834 C JP 4217635 A JP 7029960 B PL 289475 A1 SK 281452 B6 SU 1838289 A3 US 5262443 A ZA 9102025 A	20-09-1991 15-06-1996 24-12-1992 19-09-1991 20-09-1991 30-10-1991 15-10-1991 18-07-1996 24-10-1996 25-09-1991 16-10-1996 19-03-1996 07-08-1992 05-04-1995 24-02-1992 12-03-2001 30-08-1993 16-11-1993 24-12-1991
EP 1010464	A	21-06-2000	JP 3118565 B2 JP 2000176287 A EP 1010464 A2	18-12-2000 27-06-2000 21-06-2000

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/13942

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1010464	A	US 6342538 B1	29-01-2002
US 6303535	B1	16-10-2001	
		DE 19933348 A1	08-02-2001
		BR 0002918 A	03-04-2001
		FR 2796315 A1	19-01-2001
		JP 2001062311 A	13-03-2001
		SG 86419 A1	19-02-2002